

## NATROJAROSITE FROM KUNDIP, PHILLIPS RIVER GOLDFIELD.

By

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Before entering upon a description of the mineral Natrojarosite from Kundip and its mode of occurrence, it will be well to give a short outline of the history of the species Natrojarosite and its potassium homologue, Jarosite. This is advisable since, whilst both are comparatively rare minerals, the subject of this paper is so little known that even its name does not appear in any but the most recent text books.

### HISTORICAL.

1838. C. F. Rammelsberg described a "Yellow Iron Ore" (Gelbeisenerz) from Luschitz, Bohemia, where it occurred in brown coal. The composition was that of a basic sulphate of iron and potassium, for which the author calculated the formula,  $K_2O.4Fe_2O_3.5SO_3.9H_2O$ .—Pogg. Annal., 43, 132.

Later in the same year, Scheerer published an analysis of a similar mineral occurring in alun-slate at Modum, Norway. In this, sodium entirely replaced the potassium of the Luschitz mineral, the calculated formula being  $Na_2O.4Fe_2O_3.5SO_3.9H_2O$ .—Pogg. Annal. 45, 188.

1847. J. A. F. Breithaupt first used the specific name Jarosite for the basic potassium iron sulphate from Sierra Almegrera, Spain, and other similar minerals of rhombohedral crystallisation.--Berg. u. Hutt. Zeit. 6, 68.

1866. A yellow mineral from Paillieres, France, thought to be a basic sulphate of iron without alkalies, named Pastreite by Dr. Normann.—Verhan. n.-h. Ver. Rheinl., 17.

1864-1890. Typical potash-bearing Jarosite, described by various authors from Spain, Saxony, Urals, Arizona, Colorado, Utah, Mexico, and Peru.

1893. W. P. Hadden described as Jarosite a mineral occurring in auriferous quartzite at the Buxton Mine, Lawrence Co., South Dakota. According to a subsequent recalculation of Hadden's figures this mineral contained soda, 4.86 per cent.; potash, 1.65 per cent. It was, therefore, not Jarosite but its sodium homologue.—Amer. Jour. Sci., 46, 24.

1896. Scheerer's analysis of the sodium-bearing mineral from Norway quoted by Dana under Jarosite. He gave the formula for the latter as  $K_2O.3Fe_2O_3.4SO_3.6H_2O$ .—*Sys. Min.*, VI Edit., 975.

1899. Headden's description of the sodium mineral from South Dakota quoted by Dana under Jarosite.—1st App. to *Sys. Min.*, 37.

1901. H. W. Turner recorded the occurrence at Soda Springs Valley, Nevada, of a large quantity of a golden brown micaceous mineral, which Dr. Hillebrand reported was the practically pure sodium salt corresponding to Jarosite.—*Amer. Jour. Sci.* 13, 345.

1902. Hillebrand and Penfield described, with analysis and complete crystallographic details, the yellow rhombohedral mineral from Soda Springs Valley, Nevada, collected by Turner. The analysis was that of an almost pure sodium species corresponding to Jarosite. This they recognised as being thereby distinct from Jarosite, and gave it the new specific name Natrojarosite, assigning the mineral to the Alunite Group. The formula given is  $Na_2[Fe(OH)_2]_6(SO_4)_4$ , which may be written in the same form as that given by Dana for Jarosite. They also described an identical mineral from Cook's Peak, New Mexico.—*Amer. Jour. Sci.*, 14, 211.

1903. L. J. Spencer in his "Third List of new Mineral Names" gave Hillebrand and Penfield's "Natrojarosite."—*Miner. Mag.*, 13, 373.

1910. "Pastreite" from France shown to be normal Jarosite, by Azema.—*Bull. Soc. Franc. Min.*, 33, 130.

1911. W. T. Schaller discussed the rhombohedral Alunite-Beudantite Group, including therein Jarosite and Natrojarosite.—*Amer. Jour. Sci.*, 32, 359.

From the above brief notes it is plain that Natrojarosite was first discovered in 1838 in material from Modum, Norway, but that it was at that time included in the species Jarosite. It was not till 1902 that its independent specific character was recognised and the present name given to it.

## OCCURRENCE.

Natrojarosite has previously been recorded from the following four localities:—

Modum, Norway.

Lawrence Co., South Dakota.

Soda Springs Valley, Nevada.

Cook's Peak, New Mexico.

A search has failed to reveal any record of its discovery in Australia. To the locality list given, however, must now be added as a new locality, Kundip, in the Phillips River Goldfield of this State.

In February, 1914, three parcels of oxidised gold ore, amounting altogether to 172 tons, were sent in to the State Smelter, at Ravens-thorpe, near Kundip, from the "O.T." Tribute on the Harbour View Mineral Lease, at Kundip. This ore, when "bedded," showed a number of light yellow fragments, which proved to consist largely of ferrie oxide and sulphuric oxide, and were afterwards identified as Natrojarosite. The total quantity of this mineral was estimated at well under one per cent. The parcel of ore as a whole contained 0.52 per cent. of  $\text{SO}_3$ , which if it were all present as Natrojarosite would indicate  $1\frac{1}{2}$  per cent. of that material, but some was, no doubt, present as epsom salts and gypsum carried into the ore by the ground water, which is highly saline, as the following figures show:—

TABLE I.  
*Analyses of Kundip Groundwater.*

	Medic Mine. <sup>(1)</sup>	Flag Mine. <sup>(2)</sup>	Flag Mine.
	Parts per cent.		
$\text{CaCO}_3$ ... ..	0.0482	0.0553	0.0595
$\text{MgCO}_3$ ... ..	...	.0084	.0015
$\text{FeCO}_3$ ... ..	trace	trace	<i>Nil</i>
$\text{CaSO}_4$ ... ..	.0470	...	...
$\text{MgSO}_4$ ... ..	.3275	.1910	.2016
$\text{NaNO}_3$ ... ..	<i>Nil</i>	<i>Nil</i>	trace
$\text{MgCl}_2$ ... ..	.4088	.1627	.1896
$\text{NaCl}$ ... ..	2.5882	1.3485	1.3742
$\text{KCl}$ ... ..	...	.0198	.0129
$\text{NaBr}$ ... ..	...	.0002	.0002
$\text{NaI}$ ... ..	...	<i>Nil</i>	<i>Nil</i>
$\text{SiO}_2$ ... ..	.0032	.0024	.0026
$\text{Al}_2\text{O}_3$ ... ..	.0030	.0014	.0038
Total Solids ...	3.4259	1.7897	1.8459

The shaft from which the ore was obtained is in an area of hornblende schist near the northern corner of the Harbour View Lease<sup>3</sup>. This shaft was inspected in October, 1914, and whilst some Natrojarosite could be seen lying on the surface, none was discoverable underground. According to Mr. Charles Grant, of Kundip, the mineral is found not only in this shaft, but also in other neighbouring ones, in lenses or irregular masses in the oxidised por-

1. From shaft 10 chains W. of Natrojarosite deposit. 2. Half-mile N.E. of Harbour View Lease. 3. See G.S.W.A. Bull. 35, Plate VII., p. 96.

tion of an auriferous lode. The matrix is a gossan composed of iron hydrates, quartz, and clay. No sulphides were visible in the first shaft, but they were expected to be reached at a depth of about 140 feet. In the 103ft. and 112ft. levels and elsewhere a number of samples were taken of the soft, kaolinised rocks, which dipped at a high angle, and were dark reddish brown to white in colour. These were found to yield sulphuric oxide in small proportions from traces upwards. This has been found to be characteristic of the larger proportion of all rocks in the Phillips River Goldfield which have recently been tested. In this connection it is to be noted that several sulphides, chiefly pyrite, pyrrhotite, and chalcopyrite are widely distributed in large quantities throughout the district below the zone of oxidation.

A considerable quantity of a similar basic sulphate was found in a sample of the weathered greenstone schist carrying streaks of a yellow ochreous material from a depth of 60ft. in a new shaft on the Corona Lease in Sutherland's Gully in the Ravensthorpe Range, near Kundip, as well as in a cliff on the Jerdacuttup River. Finally on testing the ironstone used as a flux at the State Smelter and quarried in the Ravensthorpe Range at Iron Knob, 0.30 per cent.  $\text{SO}_3$  was found in poor specimens containing 62 per cent.  $\text{Fe}_2\text{O}_3$  and 10 per cent.  $\text{SiO}_2$ , and 0.52 per cent.  $\text{SO}_3$  in picked specimens containing 75 per cent.  $\text{Fe}_2\text{O}_3$  and 3 per cent.  $\text{SiO}_2$ . This ironstone represents possibly the outcrop of a large lode in which pyrites, pyrrhotite, and magnetite are abundant below water level. A similar lode, outcropping at Mt. McMahon,  $2\frac{1}{2}$  miles to the North-West, was pierced by a bore at some depth below the zone of oxidation, and portions of the core on analysis gave:—

TABLE II.  
*Sulphide Lode, Mt. McMahon, Ravensthorpe.*

	(A)	(B)
Fe	44.37 %	45.68 %
Cu	.03	.02
Ni	.06	trace
Sb	.02	.01
S	35.91	30.70
$\text{SiO}_2$	14.70	9.33
$\text{Al}_2\text{O}_3$	trace	trace
MnO	.97	1.55
CaO	.72	1.53
MgO	3.73	4.10
O etc.	traces	(7.08)
	100.51	100.00

The chief metallic constituents of A were pyrrhotite, and pyrites with traces of magnetite; of B, pyrites, pyrrhotite, and magnetite in



roughly equal proportions. The normal weathering of such material would give rise to large quantities of sulphuric acid and sulphates.

### PHYSICAL PROPERTIES.

The specimens from the Harbour View Lease consist of practically pure mineral in irregular masses from a few grammes to  $\frac{1}{4}$  kilo in weight. They are bright ochre yellow to brownish yellow in colour, dull in lustre, porous, and at times more or less cellular. They vary in coherence from very friable to moderately tough. In one specimen the mineral encloses a small vein of quartz.

An examination of the powder under the microscope discloses the fact that this is wholly in transparent crystalline grains, of which many are perfect crystals, varying in diameter from 3 to 5  $\mu$ . The crystals are disc-like, with a thickness equal on the average to one-third of the diameter. Many possess a small turbid core, the exact cause of which was not determinable. By pressing some of the powder, mounted in cedar oil, between cover-glass and slip, a number of crystals were flattened against the glass. In the more perfect crystals the outlines of upper and lower basal planes were then seen to be equilateral triangles in alternating position. As the crystals in this position proved to be singly refracting, the crystal system is evidently rhombohedral, and the form the combination of rhombohedron with two truncating basal planes. The refractive index was high, birefringence strong.

The specific gravity was determined by immersing several small fragments (previously washed in small quantities of distilled water, alcohol, and ether, *vide infra*.) in methylene iodide of density 3.32 and gradually diluting this with measured quantities of a mixture of xylol and methylene iodide of density about 1.5. The sinking point was noted as compared with that of test minerals whose specific gravity had been determined with great care. By thus interpolating between spodumene of density 3.14 and rubellite of density 3.01, the Kundip mineral was shown to have a density of 3.11 at 29° C.

The melting point was indeterminate owing to the mineral dissociating at a low temperature.

### CHEMICAL PROPERTIES.

Preliminary experiments proved, as was expected with such porous material, that about one per cent. of water-soluble salts deposited by the saline ground water (*vide supra*) were present. These were chiefly common salt and epsom salts. Further it was proved that Natrojarosite itself was apparently entirely unaffected even by long continued contact with boiling water. For analysis, therefore, a seemingly pure fragment of mineral was selected, broken to pass a 20-mesh sieve and washed rapidly with a few small lots of cold, distilled water to remove all associated salts, then in succession with

6 : 1 alcohol, absolute alcohol, and ether to remove water and ensure rapid drying at a low temperature. Finally the mineral was dried at 50° C., crushed to pass a 90-mesh sieve, and bottled. The material so prepared was found to contain 0.04 to 0.08 per cent. of hygroscopic water, and from *nil* to 0.20 per cent. of insoluble matter.

The results obtained on three separate specimens were:—

*Natrojarosite, Kundip.*

	Theory. %	A %	B %	C %	mols.
H <sub>2</sub> O ...	11.15	...	...	10.93	606
Na <sub>2</sub> O ...	6.39	...	...	6.32	102 )
K <sub>2</sub> O ...	...	...	...	.68	7 } 109
Fe <sub>2</sub> O <sub>3</sub> ...	49.42	49.99	49.98	49.86	312
FeO ...	...	...	...	.16	2
SO <sub>3</sub> ...	33.04	33.08	32.13	32.30	403
P <sub>2</sub> O <sub>5</sub> ...	...	...	...	.20	1½
	100.00			100.45	

All results in the case of "C" are the means of two concordant estimations, using only vessels of quartz and platinum, and reagents of "Guaranteed Reagent" quality, whose purity had been confirmed.

None of the water was removed at temperatures up to 150°C., from which it would appear that none of it is water of crystallisation.

The empiric formula for minerals of the Alunite Group is



For Natrojarosite this becomes



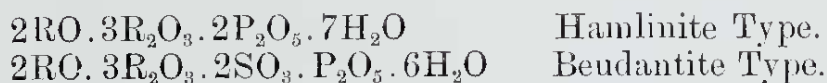
This may be written (Hillebrand and Penfield)



The results obtained for the Kundip mineral give slightly high results for alkalies and ferric oxide and correspondingly low results for water and sulphuric oxide. The departure from the theoretical ratios is, however, quite small, viz.:—

	Theory mols.	Found mols.
H <sub>2</sub> O ...	6.00	5.94
Na <sub>2</sub> O ...	1.00	1.07
Fe <sub>2</sub> O <sub>3</sub> ...	3.00	3.06
SO <sub>3</sub> ...	4.00	3.95

The presence of traces of phosphoric oxide (previously observed in similar minerals) and of ferrous oxide is doubtless to be ascribed to the co-existence of an isomorphous mineral of the Hamlinite or Beudantite type, viz.:—



The molecular weight and molecular volume for the Kundip mineral and other minerals of the group are:—

	Molecular Weight.	Specific Gravity.	Molecular Volume.
Natrojarosite, Kundip	971.5	3.11	312.3
Natrojarosite, pure ...	969.4	(3.10)	(312.4)*
Jarosite ... ..	1001.6	3.20	313.0
Alunite ... ..	829.2	2.66	311.8

\* Assumed. being mean of figures for Jarosite, Alunite, and the Kundip mineral. From this figure the specific gravity of pure Natrojarosite, unknown in nature, is calculated to be 3.10.

Kundip Natrojarosite is insoluble in water. Some of the finely powdered mineral was shaken with a little cold water to dissolve the associated salt and magnesium sulphate and then washed several times on a filter with small lots of water until the filtrates gave no reaction for chlorine. Subsequent treatment with cold water yielded filtrates giving no reaction for sulphate ion with barium chloride, nor for ferric ion with ammonium sulphocyanide. On boiling with water no change could be observed in the mineral. The water remained neutral in reaction to methyl orange and litmus, and no sulphate ion could be detected in solution.

Cold, strong, hydrochloric acid (10 E) had no immediate effect, though, doubtless, complete solution would result on long continued digestion. On heating almost to boiling, solution was moderately rapid, 0.5 gramme of the mineral dissolving completely in about 15 minutes. Dilute hydrochloric acid (5 E) acted extremely slowly even when boiling.

Dilute sulphuric acid (5 E) had practically no effect even at boiling point. On concentrating the acid in contact with the mineral by evaporation on a sand bath, the powdered mineral remained almost unaffected till the acid reached the strength of about 10 E, when solution was more rapid, and was complete just short of fuming point.

The mineral is very slowly attacked by hot concentrated (16 E) nitric acid.

Boiling for a few minutes with a mixture of one part of 22 E hydrofluoric acid and two parts of 10 E sulphuric acid gave a perfect solution. This was found a convenient method of solution for the estimation of ferrous iron.

Digestion of the powdered mineral with weak caustic potash (1 E) in the cold ( $18^{\circ}\text{C}$ ) resulted in somewhat slow decomposition. The colour of the powder had changed after five minutes from yellow to orange, and after 30 minutes to light red, the colour gradually deepening. Contact with alkali of the same strength at a temperature of  $50^{\circ}\text{C}$  resulted in rapid decomposition, all  $\text{SO}_3$  and  $\text{Na}_2\text{O}$  going into solution and leaving a bulky dark red residue of ferric hydrate. The instability of the mineral towards moderately concentrated alkalis is further illustrated by the fact that if a slight excess of ammonia or fixed alkali is added to a solution of the mineral in hydrochloric acid, the resulting iron precipitate contains no trace of either sulphuric oxide or alkali.

At the suggestion of Mr. Alex. Montgomery experiments were made on the effect of the mineral on weak potassium cyanide solution, 0.2 gm. of the powdered mineral was digested in the cold with 50 cc. of a 0.5 per cent. solution of potassium cyanide. After  $1\frac{1}{2}$  hours no weakening of the solution was determinable, after two days, however, the strength of the solution was reduced by 10 per cent. This fact has an obvious bearing on the problem of successful extraction of gold from oxidised ores, in which this mineral, or a similar one, may be present without having been detected.

Effect of dry heat.—On heating the mineral for an hour at  $100^{\circ}$ , a minute loss (0.01 to 0.04 per cent.) of hygroscopic water was noted. Further successive heatings for an hour each time with rises of  $10^{\circ}$  up to  $150^{\circ}$  caused no further alteration in weight whatever. None of the water, therefore, is water of crystallisation. At a temperature below red heat, acid water was evolved and at a very low red heat fumes of  $\text{SO}_2$  were observed to come off. On heating over a meeker burner in a platinum crucible, practically constant weights were reached with a loss of 35.36 and 35.50 per cent. This is equal to all the water plus three-quarters of the sulphuric oxide. Cold water extracted sodium sulphate from this ignited mineral, the residue being practically pure ferric oxide. Blasting produced a slow reduction in weight, doubtless due to dissociation of the alkali sulphate. After 30 minutes it amounted only to 0.8 per cent., after which the process was discontinued.

On heating a small fragment of the mineral in an open bunsen flame an intense soda coloration was produced.

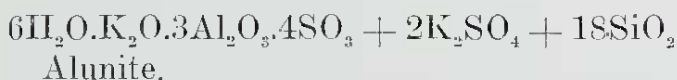
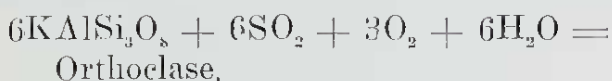
Heating in a closed tube gives white fumes which condense to a strongly acid sublimate of sulphuric acid and water, leaving a dark red residue.



## GENESIS.

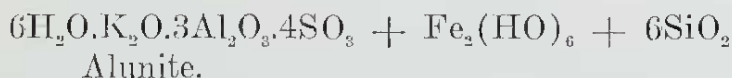
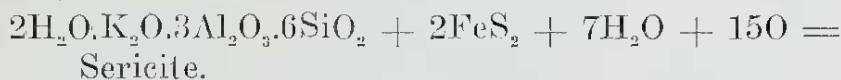
The proved chemical properties of the mineral form a basis upon which to build up the steps by which the mineral has been formed, though no theory of origin can be considered final until the deposit in which the mineral occurs has been traced below the zone of oxidation.

The genesis of alunite, the commonest mineral of this group, is usually ascribed to solfataric action on rocks containing large quantities of orthoclase. Thus:



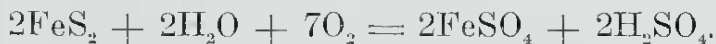
In the customary presence of other aluminous silicates, such as oligoclase, etc., no free potassium sulphate would be produced, the whole of it combining with aluminium sulphate to form alunite. It is to be noted that a mixture of sulphur dioxide and oxygen are necessary to produce this effect. Such a mixture has indeed been recorded in gases from two volcanoes, Hekla and Vulcano\*, but must be far from common in sub-surface fissures.

On the other hand alunite might well be produced by the weathering of an "alum slate" containing much sericite and pyrites or marcasite, thus:

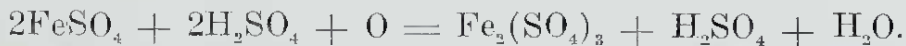


The Kundip Natrojarosite is almost certainly not the result of solfataric action, but the product of the weathering underground of pyritous ore in the presence of sodium-bearing rocks and ground waters.

The normal equation for the first stage in the weathering of pyrites† in a quartz reef or elsewhere, where easily decomposed rock silicates and carbonates do not come into action, is



With additional penetration of atmospheric oxygen, further oxidation of the ferrous sulphate takes place, thus:



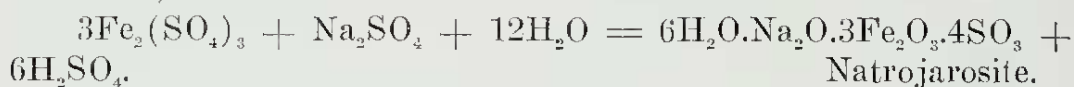
It is seen that the oxidation of ferrous sulphate to ferric sulphate reduces the acidity of the solution to one-half, thus increasing the tendency to formation of basic salts.

\* F. W. Clarke, Data of Geochemistry, Edit. II., pp. 249-251.

† Van Hise, Treatise on Metamorphism, p. 214, does not give this equation. He gives, however, five others as representing probable reactions, during the sub-surface weathering of pyrites. One of these gives  $\text{H}_2\text{S}$  and  $\text{SO}_2$ , two incompatibles, as simultaneous products of the reaction; a second gives ferric hydrate with a considerable excess of  $\text{SO}_2$ ; a third, ferric hydrate with abundant sulphuric acid! These equations appear to require some explanation.—E. S. S.

Contact of this oxidised solution with excess of alkaline ground water would, from the experiments described above (p. 53), result in the precipitation of ferric hydrates, leaving all alkali and sulphuric oxide in solution. This is the result usually observed in weathered lodes.

Many of the lodes of the Kundip district, including the one under discussion, are impregnations of amphibolites or other rocks carrying sodium-bearing silicates. Were some portion of the oxidised iron solution for some abnormal reason to remain out of the reach of the main underground circulation, the free acid would gradually attack such silicates, a neutral or faintly acid solution remaining, which contained ferric sulphate and sodium sulphate. Hydrolysis of this solution would then give rise to the formation of the basic salt Natrojarosite, since this compound is insoluble in such a solution, thus:



Perth, 12th April, 1915.